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Systematics of the odd–even effect in the resonance ionization of Os and Ti

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ABSTRACT: Measurements of the odd-even effect in the mass spectrometric analysis of Ti and Os isotopes by resonance ionization mass spectrometry have been performed for $\Delta J = +1, 0$ and -1 transitions. Under saturating conditions of the ionization and for $\Delta J = +1$ transitions odd-even effects are reduced below the 0.5% level. Depending on the polarization state of the laser large odd isotope enrichments are observed for $\Delta J = 0$ and -1 transitions which can be reduced below the 0.5% level by depolarization of the laser field.

1. INTRODUCTION

The application of resonance ionization mass spectrometry (RIMS) to accurate isotopic analysis in geo- and cosmochemistry is complicated by the presence of laser induced shifts in measured isotopic ratios. Observed effects range from 3% (Walker and Fassett 1986) to over 40% (Fairbank et al 1989, Spiegel et al. 1992) with a predominant enrichment of the odd mass isotopes. Laser induced shifts can be broadly divided into wavelength tuning effects which originate from the finite overlap of the laser spectral distribution with the absorption maxima of the different isotopes (Wunderlich et. al. 1992 a and b) and the intrinsic odd-even effects (Fairbank et al 1989, Lambropoulos et al. 1989, Payne et al. 1991, Wunderlich et al. 1992 a and b). In practical applications of RIMS to isotopic analysis intrinsic odd-even effects can be compensated for by comparison of measured isotopic ratios with a standard of known isotopic composition (Spiegel et al. 1992). However, the size of the effects makes accurate determination of isotopic ratios difficult and precludes the ready identification of material of unusual isotopic composition. Furthermore, in some systems, like in the Re-Os chronometer, there is no standard for the radiogenic isotope available.
In this study we examined the odd-even effect in the resonance ionization of Ti and Os in order to devise methods to avoid or greatly reduce the size of these effects in isotopic analysis. Os and Ti were selected because of their importance in geo- and cosmochemistry.

2. ODD-EVEN EFFECTS AND THE MEASUREMENT OF ISOTOPIC RATIOS

Intrinsic odd-even effects can be divided into selection rule effects and dynamic effects. Selection rule effects can be present when the resonance transition involves angular momentum changes $\Delta J=0$ or -1. In this case a certain fraction of the ground state M_J and M_F components will not interact with a linearly or circularly polarized laser field. Because of the increased number of agular momentum states for isotopes with nuclear spin (odd isotopes) this fraction is smaller for the odd isotopes, resulting in odd

isotope enrichment. Considering a $\Delta J=0$ transition between J=1 states, 1/3 of the ground state population does not interact with a linearly polarized laser field because of the forbidden $M_J = 0 \rightarrow M_J = 0$ transition. Upon addition of an half integer nuclear spin this selection rule is no longer in effect resulting in an enhancement of the odd isotopes. This situation is met in many resonance transitions in Ti and Os. In principle selection rule effects could be corrected by simple level counting. However, in many practical applications the laser radiation is not of a pure polarization state causing deviations of isotopic ratios obtained with this type of resonance transition from the expected values and a reduction of the odd-even effect (Wunderlich et al. 1992 a,b). Measured isotope ratios will then depend on the laser intensity, beam parameters and ion optical extraction conditions. The effects will be particularly pronounced in multistep ionization schemes with noncolinear laser beams because ionization can be produced from regions with widely different saturation of the different M_J ground state components. These considerations suggest the use of depolarized light for the excitation of the discrete resonances in RIMS. This also provides the advantage of not having to use all $\Delta J=+1$ resonance transitions.

Dynamic effects have been discussed in detail by Lambropoulos and Lyras (1989) and by Payne et al. (1991) including the effects of the laser spatial intensity distribution. Dynamic effects pertain to $\Delta J=+1$ transitions where from selection rule arguments no odd isotope enrichment should be present. A coherent and incoherent regime can be distinguished. In the first case with interaction times much smaller than the HFS coupling time a coherent superposition of HFS levels is excited. With regard to population balance ionization proceeds as if the HFS structure was absent and no odd-even effects should be observed. For interaction times much larger than the HFS coupling time and large laser bandwidhts excitation proceeds via independent HFS states. Due to the higher excited state degeneracy for isotopes with nuclear spin there will be on average more atoms in the resonance state for odd isotopes as compared to the even isotopes dending on the polarization state of the laser. This can result in a large odd isotope enrichment if the ionization is not saturated. Thus, saturation of the ionization is essential for obtaining a small odd-even effect. However, considering again the incoherent case depolarization of the resonance excitation laser should also result in an equal fraction of excited state atoms for the odd and even isotopes resulting in a large reduction of the odd-even effect.

3. EXPERIMENTS AND RESULTS

Details of the experimental set up and procedures have been described by Wunderlich et al. (1992 a). A frequency doubled pulsed laser system, thermal atomic beam and a modified quadrupole mass spectrometer were used for the RIMS experiments. Single photon 1 + 1 schemes with resonances near 40000. cm^{-1} were used for the resonance ionization of Ti and Os. The width of the HFS transition arrays for the odd Os and Ti isotpes were obtained from intracavity etalon scans. The dye laser fundamental could be operated with a bandwidth of 0.4 cm^{-1} to assure excitation of the whole HFS transition arrays.

The experiments on $\Delta J=+1$ transitions in Os and Ti were all performed in the incoherent regime, that is the pulse duration of 20 ns was much larger than the inverse HFS splitting. Results from a series of

Table 1. Odd-even effects in Os and Ti isotope ratios for $\Delta J=+1$ transitions. Numbers in paranthesis indicate the 1σ error

Resonance State (cm^{-1})	$\delta^{47}Ti$ (‰)	$\delta^{49}Ti$ (‰)	$\delta^{189}Os$ (‰)	mode
39405.9			-3.4 (5)	sat
38544.4	-14 (12)	+2.8 (11)		sat
37851.5	+35 (11)	+4.6 (11)		sat
38159.5	+60 (15)	+144 (23)		nsat

measurements are given in Table 1. The isotopic ratios have been corrected for mass fractionation and are given in the per mil deviation from their standard values (δ-values) (Os ratios: Creaser et al. 1991, Ti ratios: Niederer et al. 1981). Reference isotopes were ^{46}Ti and ^{190}Os. Mode indicates saturating (sat) or nonsaturating (nsat) conditions of the ionization.

Under saturating conditions of the ionization no odd-even effect for Os is seen. This result differs from the one obtained by Walker and Fassett (1986) where a 3% enrichment in ^{189}Os was observed. With exception of the δ^{47}Ti = 35 value, the Ti results obtained under saturating conditions are compatible with the absence of odd-even effects. The values obtained under nonsaturating conditions show a considerable increase in the odd isotope ratios consistent with the arguments given above. The higher vavalue of δ^{49}Ti may be caused by the larger number of excited state components in ^{49}Ti compared to ^{47}Ti (I=5/2 for ^{47}Ti and I=7/2 for ^{49}Ti).

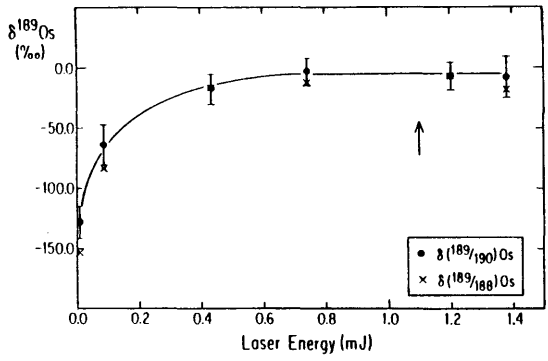

Fig.1. Power dependence of ^{189}Os/^{188}Os.

The power dependence of the ^{189}Os/^{190}Os and ^{189}Os/^{188}Os ratios measured for the ΔJ=+1 transition is shown in Fig.1. The arrow indicates the onset of ionization saturation. The ratios are constant for laser intensities larger than half the ionization saturation intensity and agree very well with the standard ratios after mass fractionation correction. The maximum laser intensity in the experiment was 5 x 10^7 Watt/cm^2 so that the constancy of the isotopic ratios can not be explained by laser bandwidth effects.

Selection rule and polarization effects were studied on ΔJ =0 and -1 transitions in Os and Ti. Some degree of depolarization was generated by passing the expanded laser beam through a quartz window exposed to localized stress creating a random amount of birefringence across the laser beam diameter. P_{ell} is the ratio of the maximum and minimum intensity measured in two orthogonal directions of a linear polarizer positioned behind the experiment chamber. In Table 2. odd-even effects obtained for different values of P_{ell} are listed in δ-values. With exception of the Os ΔJ=0 (40361.9 cm^{-1}) result odd-even effects are absent for a large degree of depolarization of the laser beam, P_{ell} =27. The Ti result is markedly different from the results obtained by Spiegel et al. (1992) in a multistep ionization scheme with a series of ΔJ=0 transitions where effects up to δ^{47}Ti = 350 were observed. Based on selection rules we calculate a maximum odd isotope effect of δ^{47}Ti = 225 for linearly polarized radiation for this type of transition.

Table 2. Polarization dependence of the odd-even effect for ΔJ=0 and ΔJ=-1 transition in Os and Ti. Numbers in paranthesis indicate the 1σ error

P_{ell}	δ^{47}Ti (ΔJ=0)	δ^{189}Os (ΔJ=-1)	δ^{189}Os (ΔJ=0)
220	+137 (10)	+57 (8)	+89 (10)
27	+2.7 (10)	-1.3 (13)	+36 (8)

Thus we suggest that the size of the odd-even effect was most likely increased in the final autoionizing step with an additional ΔJ=-1 transition. The residual odd isotope enrichment of 3.6% for the Os ΔJ=0 as compared to the ΔJ=-1 resonance transition (39406.cm^{-1}) with P_{ell} =27 appears unusual considering the much larger oscillator strength of the ΔJ=0 transition (i.e. 0.3 compared to 0.003). As such a small

admixture of elliptical polarization should saturate the M_J=0 to M_J=0 transition and no odd isotope enrichment should be observed.

The effect of the spatial intensity distribution in the laser beam on odd-even ratios is shown in Table 3. The $^{189}Os/^{190}Os$ ratio was measured for different focussing conditions for the ΔJ=-1 resonance transition and with P_{ell} = 27. The confocal parameter in all experiments was larger than the logitudinal extend of the ion collection region. It is seen that strong focussing results in a large reduction of the odd isotope enrichment as could be expected from the arguments given above. All experiments were carried out under saturating conditions of the ionization. The ionization rate R_I was smaller than the HFS splitting so that the ionization was generated from an incoherent superposition. In case the HFS splitting is much smaller than R_I it can be expected that odd-even effects will be absent for ΔJ=0 and -1 transitions.

Table 3. Dependence of $\delta^{189}Os$ on focussing conditions for P_{ell} = 27.

ΔJ	f = 100cm	f =35
-1	74 (11)	-1.3 (13)
0	57 (16)	36 (8)

4. SUMMARY AND CONCLUSIONS

Odd-even effects in the isotopic analysis of Os and Ti by RIMS were studied. It could be shown that under saturating conditions of the ionization odd-even effects were absent for ΔJ=+1 transitions or could be reduced below the 1% level. For ΔJ=0 and -1 transitions it was shown that the odd-even effects could be strongly reduced depending on the polarzation state and focussing conditions of the laser. In particular for one ΔJ=0 and -1 transition effects were absent for a large degree of depolarization and strong focussing conditions. The results given here show that with a careful choice of the experimental parameters it is possible to obtain an accuracy better 0.5% for isotopic analysis with RIMS.

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